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Vaporization and Thermodynamic Activities in $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$, $x = 0.05$, 0.10, and 0.15, Investigated by Knudsen Effusion Mass Spectrometry

Dong-Hyun Peck,[a] Miroslaw Miller,[b] and Klaus Hilpert[a]

[a]*Research Center Jülich, Institute for Materials and Processes in Energy Systems, 52425 Jülich, Germany*
[b]*Wroclaw University of Technology, 50 370 Wroclaw, Poland*

Vaporization of the perovskite phase $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$, $x = 0.05$, 0.10, and 0.15, was investigated by the use of Knudsen effusion mass spectrometry in the temperature range 1900 to 2100 K. The partial pressures of Cr(g), CrO(g), CrO_2(g), CaO(g), Sr(g), SrO(g), and LaO(g) were determined for all the samples investigated at 2000 K. The partial pressure of O_2(g) was, in addition, evaluated from the gaseous equilibria. The equilibrium partial pressures were used for the calculation of thermodynamic activities of the components at 2000 K. The results were compared with thermodynamic data for $La_{1-x}M_xCrO_{3-\delta}$, M = Ca,Sr.

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Acceptor-doped perovskites of the composition $La_{1-x}M_xCrO_{3-\delta}$, M being a second group element, show high electrical conductivity, high melting point, and excellent chemical stability under reducing and oxidizing atmospheres. These refractory electric conducting ceramic materials are of great practical interest for the production of electrodes in magnetohydrodynamic (MHD) generator channels,[1] heating elements in high temperature furnaces, and interconnects in solid oxide fuel cells (SOFCs).[2,3] Knowledge of high temperature chemistry and thermodynamics of these materials under oxidizing and reducing conditions is necessary in order to understand the degradation and corrosion processes which are possible in the above-mentioned systems. For example, the vaporization processes in the different atmospheres at the anode and cathode sides of SOFCs have to be known under operating conditions. It has been shown that chromium vaporization can lead to a rapid degradation of the electrical properties of an SOFC with a metallic interconnect.[4,5] Knowledge of the potential for decreasing this vaporization by the use of a doped $LaCrO_3$ ceramic interconnect is therefore necessary. From the potential materials, a perovskite phase, $La_{1-x}M_xCrO_{3-\delta}$, doped with the second group element (M = Ca or Sr) was used for this purpose.[6]

We reported previously on a vaporization study of ternary phases $La_{1-x}Ca_xCrO_{3-\delta}$[7] and $La_{1-x}Sr_xCrO_{3-\delta}$.[8] These phases vaporize incongruently by depletion of the gaseous chromium oxides. The activity of Cr_2O_3 in the ternary chromia-poor perovskites increases with increasing content of Ca or Sr in the A sublattice of perovskite. Thermodynamic activities of the II group element oxides in the doped lanthanum chromate is, in both cases, relatively high. This is disadvantageous because of the possible formation of alkaline earth carbonates from the alkaline earth oxides in the perovskite phase and CO_2(g), especially $SrCO_3$ can be formed, if H_2/CO anode gases are used.[9]

The present paper reports on the experimental investigations on vaporization of the $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$ samples doped by two second group elements. The aim of the work was to clarify whether the codoped perovskite phase has better thermodynamic properties in comparison to the ternary phases doped only by one alkaline earth metal. In particular, activities of Cr_2O_3 and of CaO and SrO were to be determined and compared to those obtained for the two ternaries.

Experimental

Three samples of the compositions $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$, $x = 0.05$, 0.10, and 0.15 (A, B, and C in Table I) were prepared by melting and decomposition of the respective nitrates. $La(NO_3)_3 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, and $Cr(NO_3)_3 \cdot 9H_2O$ (each reagent grade) supplied by Merck, Darmstadt, Germany, were used as starting materials. The samples were sintered at temperatures between 1473 and 1673 K for 10 h. The phase composition of the samples was checked by X-ray diffraction (XRD) investigations. Chemical analysis of samples after preparation was performed by means of the inductively coupled plasma-Auger electron spectroscopy (ICP-AES) method using the 34000-459B apparatus from Fisons/ARL, Switzerland (see Table I). The uncertainty of the La, Cr, and Sr contents in the samples amounted to ±3%.

The vaporization studies of the $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$ phases were carried out by Knudsen effusion mass spectrometry (see, *e.g.*, Ref. 10, 11). The instrument of the MAT 271 type was supplied by Finnigan MAT, Bremen, Germany, and is completely computer controlled. The vapor species were ionized with an emission current of 1 mA and an electron energy of 50 eV. A Knudsen cell made of tungsten and lined completely with iridium was employed in the measurements. Temperatures were measured by an automatic pyrometer of the ETSO-U type supplied by Dr. Georg Maurere GmbH, Kohlberg, Germany, and calibrated using the melting points of silver, gold, and platinum. Chemical analysis of the samples after the vaporization study was performed by means of ICP-AES and results are reported in Table I as well.

Results

Ionic species and their assignment to neutral precursors.—The ion species Cr^+, CrO^+, CrO_2^+, CaO^+, Sr^+, SrO^+, La^+, and LaO^+ were detected in the mass spectrum of the vapor over the different $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$ samples. They were identified by their masses, by the shutter effect, and by their isotope abundances. The assignment of the ions to their neutral precursors has been reported in Ref. 7, 8 on vaporizing the ternary phases $La_{1-x}M_xCrO_{3-\delta}$.

The intensities of the ions were measured in the course of runs 1-8 for three different $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$ samples of the compositions given in Table I. The runs were performed in the temperature range 1900 to 2100 K. The starting temperature was adjusted at the end of each run in order to check the reproducibility of the vapor pressure measurements. In runs 1, 3, 5, and 7, new sample materials were taken for the study. At the beginning of these runs, the decreasing intensities of the Cr-containing ions were observed at constant temperature due to a change of the chemical composition of the perovskite phase. Time-independent intensities were obtained after 24 to 90 h depending on the sample composition. This was checked for about 20 h. The measurements were carried out in this time period. The depletion of Cr_2O_3 resulted in the formation of the second phase (probably La_2O_3 or Ruddlesden-Popper phase) in addition to the Cr_2O_3-poor perovskite. The intensities for runs 1, 3, 5, and 7 were measured after adjusting time-independent partial pressures. The XRD patterns of the samples after the vaporization measurements did not show the existence of any other phase in addition to perovskite, probably because the Cr_2O_3 loss during these vaporization measurements was too small. Plots showing the decrease of the

Table I. Nominal chemical composition of the $La_{0.8}Sr_{0.2-x}Ca_xCrO_{3-\delta}$ samples in runs 1-8 and results of the chemical analysis of the samples before and after vaporization study (uncertainty ±3%).

Sample	Runs		x (CaO)	x (SrO)	x ($1/2Cr_2O_3$)	x ($1/2La_2O_3$)
A	1, 2, 3, 4	nominal	0.025	0.075	0.500	0.400
		chemical analysis before KEMS	0.025	0.074	0.500	0.401
		chemical analysis after run 2	0.025	0.071	0.487	0.416
		chemical analysis after run 4	0.025	0.070	0.492	0.413
B	5, 6	nominal	0.050	0.050	0.500	0.400
		chemical analysis before KEMS	0.051	0.051	0.497	0.401
		chemical analysis after run 6	0.050	0.050	0.485	0.415
C	7, 8	nominal	0.075	0.025	0.500	0.400
		chemical analysis before KEMS	0.075	0.025	0.498	0.402
		chemical analysis after run 8	0.077	0.026	0.487	0.410

ion intensities as function of the time are shown in Ref. 7 and 8 on studying the perovskite phases $La_{1-x}Ca_xCrO_{3-\delta}$ and $La_{1-x}Sr_xCrO_{3-\delta}$.

Runs 2, 4, 6, and 8 were performed using the samples from previous measurements. Before these runs, samples were ground in an agate mortar to prevent diffusion-controlled vaporization in a subsequent experiment. All the ion intensities remained stable at constant temperature from the beginning of these runs. The measured ion intensities corrected for isotopic distribution are listed in Table II for run no. 1 as an example.

Partial pressures.—Partial pressures $p(\mathrm{i})$ of species i at temperature T were obtained from the equation

$$p(\mathrm{i}) = k\frac{\sigma(\mathrm{Pt})}{\sigma(\mathrm{i})}T\sum I(\mathrm{i}) \qquad [1]$$

where k and $\Sigma I(\mathrm{i})$ are, respectively, the pressure calibration factor and the sum of the intensities of the ions originating from the same neutral precursor i. $\sigma(\mathrm{i})$ is the ionization cross section of the species i. The values of the relative ionization cross section ratios $\sigma(\mathrm{Pt})/\sigma(\mathrm{i})$ given in parentheses were used for the following gaseous species i: Cr (1), CrO (0.71), CrO_2 (0.26), LaO (2.51), CaO (6.65), Sr (0.73), and SrO (0.52). They were obtained on the basis of the experimental cross section ratios $\sigma(\mathrm{MO})/\sigma(\mathrm{M}) = 0.71$ and $\sigma(\mathrm{MO_2})/\sigma(\mathrm{MO}) = 0.36$ selected from the data reported by Drowart[12] for transition metals M. The ionization cross section ratio $\sigma(\mathrm{Pt})/\sigma(\mathrm{Cr}) = 1.0$, based on the experimental cross section ratios $\sigma(\mathrm{Cr})/\sigma(\mathrm{Au}) = 1.5$[13] and $\sigma(\mathrm{Pt})/\sigma(\mathrm{Au}) = 1.46$,[14] was used for the determination of $\sigma(\mathrm{Pt})/\sigma(\mathrm{i})$ given in Eq. 1. The ionization cross sections of LaO were obtained by using the value $\sigma(\mathrm{La})/\sigma(\mathrm{Cr}) = 3.54$.[15] The ionization cross section of SrO and CaO were obtained from the subsequently performed vaporization experiments of pure SrO(s), CaO(s), and Pt(s) by using Eq. 1 and partial pressures of the pure substances.[16]

Pressure calibration was carried out by vaporizing pure Pt at its melting temperature of 2042 K.[17] As an example, the pressure calibration constant $k = 3.86 \times 10^{-9}$ Pa s K^{-1} resulted for run 1. Partial pressures were evaluated by the use of Eq. 1 for each measurement temperature. In Fig. 1 we show, as an example, partial pressures of vapor species obtained in run 1 for sample A. Table III gives the partial pressures of the different species interpolated to 2000 K in the measurements. The O_2 partial pressures were computed from the equilibrium constant of the reaction $\mathrm{CrO(g)} = \mathrm{Cr(g)} + \frac{1}{2}\mathrm{O_2(g)}$ by using the measured Cr(g) and CrO(g) partial pressures as well as the values of the equilibrium constant of this reaction from the literature.[18] The formation of the ion CrO^+ from the gaseous species CrO(g) and CrO_2(g) by fragmentation was taken into account as described in Ref. 7.

Thermodynamic activities.—The determination of the thermodynamic activity of Cr_2O_3 in $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$(s) was carried out by vaporizing pure Cr_2O_3 before and after the measurement of a sample. The equilibria

Table II. Ion intensities (in s^{-1}) at different temperatures, corrected for the isotopic distributions obtained in run 1, and assignment of the ions to neutral molecules.

	Cr(g)	CrO(g)	CrO_2(g)	LaO(g)		Sr(g)	SrO(g)	CaO(g)
T/K	Cr^+	CrO^+	CrO_2^+	La^+	LaO^+	Sr^+	SrO^+	CaO^+
1906	1.56×10^3	1.21×10^2	4.72×10^1	6.2	1.74×10^1	1.23×10^3	5.14×10^1	8.6
1920	2.06×10^3	1.53×10^2	6.74×10^1	1.20×10^1	3.06×10^1	1.66×10^3	7.42×10^1	9.9
1934	2.64×10^3	2.30×10^2	9.12×10^1	1.38×10^1	3.35×10^1	2.06×10^3	1.08×10^2	1.38×10^1
1941	3.15×10^3	2.96×10^2	9.97×10^1	1.76×10^1	4.66×10^1	2.60×10^3	1.17×10^2	1.57×10^1
1948	3.36×10^3	3.13×10^2	1.13×10^2	1.99×10^1	4.79×10^1	2.67×10^3	1.56×10^2	2.27×10^1
1962	4.06×10^3	4.03×10^2	1.46×10^2	2.12×10^1	6.89×10^1	3.26×10^3	1.80×10^2	2.18×10^1
1979	5.15×10^3	5.30×10^2	2.16×10^2	3.47×10^1	1.01×10^2	4.09×10^3	2.52×10^2	3.56×10^1
1995	6.58×10^3	6.76×10^2	2.54×10^2	5.04×10^1	1.42×10^2	5.09×10^3	3.66×10^2	4.33×10^1
2010	8.22×10^3	9.08×10^2	3.34×10^2	6.10×10^1	1.75×10^2	6.11×10^3	4.48×10^2	4.92×10^1
2030	1.04×10^4	1.20×10^3	4.29×10^2	7.97×10^1	2.61×10^2	7.76×10^3	5.83×10^2	7.51×10^1
2049	1.29×10^4	1.48×10^3	6.01×10^2	1.03×10^2	3.08×10^2	9.48×10^3	7.69×10^2	7.98×10^1
2053	1.31×10^4	1.55×10^3	6.81×10^2	1.21×10^2	3.69×10^2	1.02×10^4	8.27×10^2	1.01×10^2
2066	1.57×10^4	1.95×10^3	7.93×10^2	1.41×10^2	4.18×10^2	1.19×10^4	9.65×10^2	1.15×10^2
2077	1.91×10^4	2.32×10^3	9.43×10^2	1.69×10^2	5.60×10^2	1.38×10^4	1.27×10^3	1.55×10^2
2090	2.34×10^4	3.18×10^3	1.24×10^3	2.14×10^2	6.96×10^2	1.69×10^4	1.61×10^3	2.10×10^2
2097	2.41×10^4	3.39×10^3	1.42×10^3	2.69×10^2	8.98×10^2	1.86×10^4	1.96×10^3	2.37×10^2
2103	2.82×10^4	4.09×10^3	1.61×10^3	2.73×10^2	8.63×10^2	2.01×10^4	2.04×10^3	2.59×10^2

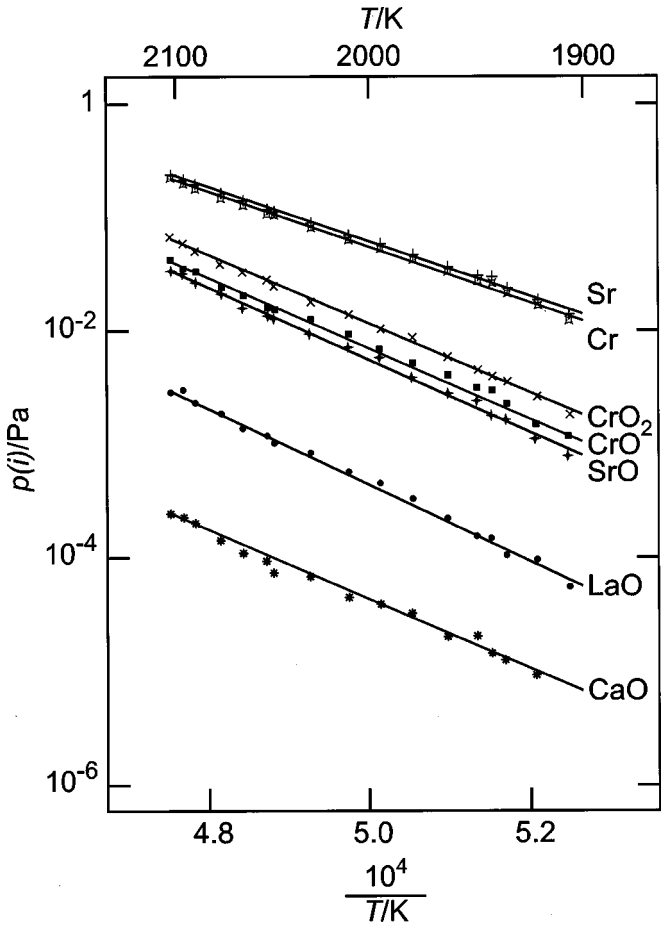

Figure 1. Partial pressures on vaporizing a sample A of the composition $La_{0.80}Sr_{0.15}Ca_{0.05}CrO_{3-\delta}$(A) in run 1.

$$\underline{Cr_2O_3}(\underline{s}) = CrO(g) + CrO_2(g) \quad [2]$$

and

$$\underline{Cr_2O_3}(\underline{s}) + Cr(g) = 3CrO(g) \quad [3]$$

were evaluated from the measurements with the sample materials and pure Cr_2O_3(s). $\underline{Cr_2O_3}(\underline{s})$ means Cr_2O_3(s) in $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$(s) and pure Cr_2O_3(s). The following equations for the thermodynamic activity resulted by considering $K_p^o(2)$ and $K_p^o(3)$ for Cr_2O_3 and for $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$(s) (see Ref. 19)

$$a(Cr_2O_3,2) = \frac{\Sigma I(CrO)[\Sigma I(CrO_2)]}{\Sigma I^0(CrO)[\Sigma I^0(CrO_2)]} \quad [4]$$

and

$$a(Cr_2O_3,3) = \frac{\Sigma I(CrO^+)^3[\Sigma I^0(Cr^+)]}{\Sigma I^0(CrO^+)[\Sigma I(Cr^+)]} \quad [5]$$

where I^0(i) denotes the ion intensities detected for pure Cr_2O_3. Thermodynamic activities were obtained for each of the measurement temperatures of runs 1 to 8 by substituting the measured ion intensities for the samples and the pure Cr_2O_3 in Eq. 4 and 5. The intensities for pure Cr_2O_3 were measured in the temperature range of 1950 to 2050 K, which corresponds to the temperature ranges of runs 1 to 8. The difference between the activity values obtained by the use of Eq. 4 and 5 at 2000 K was in each case less than 7%. The averages of the activities obtained by the two methods were taken as selected values.

Activities of SrO and CaO were calculated by comparing the ion intensity of MO^+ in the mass spectrum of the sample and of pure MO(s) and by using the equation

$$a(MO) = I(MO^+)/I^0(MO^+) \quad [6]$$

The vaporization of pure CaO was investigated in the temperature range of 1947 to 2272 K. The vaporization of pure SrO was investigated in the temperature range of 1721 to 1974 K. Therefore, an extrapolation of the ion intensities I^0(i) was used to determine the thermodynamic activities of SrO in $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$(s) at 2000 K.

The thermodynamic activity of La_2O_3 was obtained by the use of the following equilibrium as described in Ref. 7

$$1/2\underline{Cr_2O_3}(s) + LaO(g) = 1/2\underline{La_2O_3}(s) + CrO(g) \quad [7]$$

where oxides in $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$(s) are underlined. If the intensity ratio $I(LaO^+)/\{I(CrO^+)$ from CrO(g)$\}$ was measured for the sample with the known activity of Cr_2O_3, the activity of La_2O_3 could be computed from the relationship

$$a(La_2O_3) = K^2\left[\frac{I(LaO^+)}{\{I(CrO^+) \text{ from } CrO(g)\}}\right]^2 a(Cr_2O_3) \quad [8]$$

where

$$K = \frac{\{I(CrO^+) \text{ from } CrO(g)\}}{I(LaO^+)}\sqrt{\frac{a(La_2O_3)}{a(Cr_2O_3)}} = 40.6 \pm 2.0 \quad [9]$$

was determined by us previously in studying $LaCrO_3$(s) by Knudsen effusion mass spectrometry.[19]

Table IV summarizes the thermodynamic activities of the components in $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$(s) at 2000 K obtained in runs

Table III. Partial pressures over the different CaO-SrO-Cr_2O_3-La_2O_3 samples at 2000 K.

					p(i)/Pa				
Run	Sample	p(Cr)	p(CrO)	$p(CrO_2)$	p(Sr)	p(SrO)	p(CaO)	p(LaO)	$p(O_2)$
1	A	5.27×10^{-2}	6.88×10^{-3}	1.08×10^{-2}	5.55×10^{-2}	5.52×10^{-3}	3.88×10^{-5}	4.25×10^{-4}	1.57×10^{-4}
2	A	5.64×10^{-2}	7.34×10^{-3}	1.10×10^{-2}	5.39×10^{-2}	5.20×10^{-3}	4.33×10^{-3}	4.14×10^{-4}	1.55×10^{-4}
3	A	5.16×10^{-2}	7.80×10^{-3}	1.39×10^{-2}	4.93×10^{-2}	5.35×10^{-3}	4.02×10^{-5}	3.45×10^{-4}	2.10×10^{-4}
4	A	4.86×10^{-2}	7.13×10^{-3}	1.20×10^{-2}	5.33×10^{-2}	5.22×10^{-3}	3.74×10^{-5}	4.24×10^{-4}	1.98×10^{-4}
5	B	6.29×10^{-2}	1.04×10^{-2}	1.81×10^{-2}	2.63×10^{-2}	3.56×10^{-3}	7.60×10^{-5}	2.58×10^{-4}	2.49×10^{-4}
6	B	5.67×10^{-2}	8.73×10^{-3}	1.48×10^{-2}	3.02×10^{-2}	3.84×10^{-3}	7.78×10^{-5}	3.36×10^{-4}	2.18×10^{-4}
7	C	6.51×10^{-2}	1.16×10^{-2}	2.21×10^{-2}	9.26×10^{-3}	2.04×10^{-3}	1.14×10^{-4}	1.62×10^{-4}	2.92×10^{-4}
8	C	6.69×10^{-2}	1.13×10^{-2}	1.98×10^{-2}	1.06×10^{-2}	2.00×10^{-3}	1.07×10^{-4}	1.92×10^{-4}	2.65×10^{-4}

Table IV. Chemical activities of Cr_2O_3, La_2O_3, CaO, and SrO at 2000 K in the Cr_2O_3-poor perovskite phase $La_{0.8}Sr_{0.2-x}Ca_xCrO_{3-\delta}$.

Run	Sample	x	$a(Cr_2O_3)$	$a(La_2O_3)$	a(CaO)	a(SrO)
1	A	0.05	2.78×10^{-3}	0.213	0.255	0.210
2	A	0.05	2.91×10^{-3}	0.202	0.285	0.221
3	A	0.05	3.87×10^{-3}	0.160	0.264	0.211
4	A	0.05	3.10×10^{-3}	0.225	0.245	0.206
5	B	0.10	7.09×10^{-3}	0.0900	0.502	0.141
6	B	0.10	4.75×10^{-3}	0.151	0.512	0.151
7	C	0.15	9.59×10^{-3}	0.0385	0.748	6.94×10^{-2}
8	C	0.15	8.60×10^{-3}	0.0509	0.704	6.81×10^{-2}

1-8. Figure 2 shows the thermodynamic activities for the Cr_2O_3-poor phase boundary of the perovskite phase as a function of the Ca content.

Discussion

A phase diagram of the SrO-CaO system was investigated by Roth.[20] Above 900°C, both oxides form a solid solution throughout all the composition range. Our previous studies on ternary diagrams of MO-Cr_2O_3-La_2O_3 showed that the perovskite $La_{1-x}M_xCrO_{3-\delta}$ phase remains stable on doping by M atoms under low oxygen pressure at 1873 K up to $x = 0.22$ for M = Ca,[21] and up to $x = 0.31$ for M = Sr.[22] It was, therefore, expected that both oxides can be doped simultaneously into the La sublattice of the $LaCrO_3$ perovskite. The present study showed, in addition, that it is possible to replace Sr by Ca on the La perovskite sublattice at least up to 15 mol %.

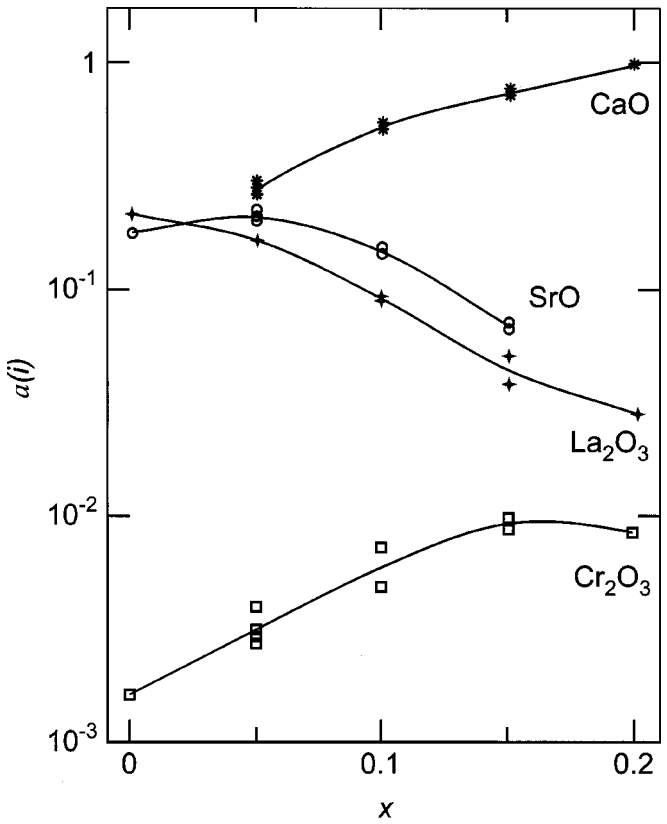

Figure 2. Thermodynamic activities of the components in the Cr_2O_3-poor $La_{0.80}Sr_{0.2-x}Ca_xCrO_{3-\delta}$(s) phase at 2000 K as a function of the Ca content in perovskite.

The perovskite composition in the study was chosen on the basis of the composition used in SOFC technology, which is typically $x = 0.15$-0.20. As shown in Fig. 2, thermodynamic activities of all the components can be expected on the basis of thermodynamic data obtained by us for the ternary perovskite phases. The activity of Cr_2O_3 is increased by increasing the Ca content in the perovskite. Partial replacement of Sr atoms by Ca can be advantageous due to (*i*) lower SrO activity and (*ii*) better sinterability of the perovskite. Lower activity of SrO can prevent carbonate formation on the anode side of SOFC. The CaO content is known to improve the sinterability of lanthanum chromate due to formation of intermediate liquid calcium chromate phase.[23]

Probable overall errors were not evaluated for the partial pressures given in this paper since it is difficult to estimate reasonable uncertainties for the ionization cross sections of gaseous oxide species. It should be noted that the determination of thermodynamic activities obtained in the study do not depend on the ionization cross sections but only on ion intensity ratios. This leads to comparatively small uncertainties for the thermodynamic activities. These uncertainties were estimated as ±15% (Cr_2O_3), ±15% (CaO), ±30% (SrO), and ±30% (La_2O_3) for the activities of components given in parenthesis. The stability of the calibration constant, the statistical scatter, the uncertainty of the *K* value in Eq. 9 and the extrapolation of ion intensities up to 2000 K performed for calibration measurements of pure SrO vaporization were considered in this estimation. The absolute uncertainty of the temperature measurement estimated as ±8 K was used in the error computation for the thermodynamic activities.

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